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<p>(54) Title: PROCESS TO MAKE INITIATOR COMPOSITIONS COMPRISING POLYVINYL ALCOHOL AND SURFACTANT</p> <p>(57) Abstract</p> <p>A process to make suspensions of thermally labile organic compounds in water is provided. The suspensions comprise at least one polyvinyl alcohol with an average degree of hydrolysis from 60 to 80 % and at least one non-ionic surfactant with an average HLB value from 14.5 to 20.0, and are suitable for use in polymerization processes. The organic compounds in the suspensions preferably have a particle size distribution where the d₉₀ is less than 20 μm. The particle size distribution of the thermally labile organic compound and the specific ingredients enable the production of chemically as well as physically storage stable suspensions that combine a high compound concentration and a low viscosity. When used in vinyl chloride polymerization processes, the suspensions ensure a low fish eye level and good electrical properties, without adversely affecting the PVC's porosity and bulk density.</p>		

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PROCESS TO MAKE INITIATOR COMPOSITIONS COMPRISING
POLYVINYL ALCOHOL AND SURFACTANT

5 Introduction

The present invention relates to a process to make storage stable and low-viscous aqueous suspensions comprising thermally labile organic compounds, at least one polyvinyl alcohol, and at least one non-ionic surfactant, to suspensions that can be obtained by this process, and to the use of these suspensions in polymerization processes.

Background of the invention

15

Water-based suspensions are well-known as safe formulations for thermally labile organic compounds such as organic peroxides and azo-initiators. Such formulations are known for their ease of handling, allowing automation of the polymerization processes in which they are used as a source of free radicals.

US 4,039,475 and US 4,092,470 describe the preparation and use, in the polymerization of vinyl chloride monomer, of initiator suspensions which contain a combination of two non-ionic emulsifiers., viz. one with an HLB value not higher than 12.5 and one with an HLB value not lower than 12.5. The HLB value of the exemplified emulsifier combinations is below 14.0. Alternatively, one non-ionic emulsifier with an HLB value not higher than 12.5 is combined with one anionic emulsifier. The suspensions are prepared by vigorously mixing and homogenizing the components. GB-B-2 068 009 elaborates on this concept and prescribes the use of specific

ethoxylated non-ionic emulsifiers with an HLB value above 15 in combination with a non-ethoxylated non-ionic emulsifier with an HLB value below 9.

- 5 However, the early introduction and acceptance of these suspensions was hindered by production problems, their physical instability, mostly resulting in the formation of a solid cake at the bottom and a watery layer on top of the container, their effect on the polymer production process, and/or their adverse effect on the properties of the polymer made with them, particularly
- 10 in polymerization processes where vinyl chloride monomer is used. For example, when formulating bis(4-tert-butylcyclohexyl) peroxydicarbonate in the way according to the prior art, we were not able to make a suspension that was storage stable, had the desired particle size distribution and an acceptable viscosity, without that the properties of poly vinyl chloride
- 15 produced therewith were adversely influenced.

EP-A-0 106 627 and EP-A-0 517 290 disclose a melt-process in which a solid peroxide consecutively is slurried in water, melted, emulsified in the water, and solidified, to give a stable suspension of finely divided peroxide particles. In the process a variety of emulsifiers and protective colloids may be used. Allegedly, this process alleviates some of the problems of the earlier suspensions. However, only specific initiators, i.e. ones that allow melting without excessive decomposition, can be formulated in this way. Also, even if excessive decomposition does not occur, safety considerations may be in the way of employing this process. In order to reduce decomposition of the initiators during storage and handling, US 4,552,682 proposes to add phenolic antioxidants to chemically stabilize suspensions of peroxydicarbonates. However, such antioxidants are known to interfere with the free radicals formed in the polymerization process in

which the suspensions are used and, therefore, are typically not acceptable. Hence, the use of phenolic antioxidants cannot relieve the decomposition problems that are encountered in the process of EP-A-0 106 627 and EP-A-0 517 290.

5

Thus, there has been an ongoing search for a process to make improved peroxide suspensions by means of conventional milling of the solid peroxide in the presence of water. The main focus has been on improving the physical stability of the various suspensions and/or finding a solution to 10 production problems. As a result, specific ingredients and formulations have been proposed in various documents. EP-A-0 263 619 discloses the use of specific crystalline cellulose. US 4,692,427, pertaining to suspensions of aromatic diacyl peroxides, teaches the use of magnesium aluminium silicate in combination with an alkali metal carboxymethyl 15 cellulose. JP-A-61127701 combines a non-ionic surfactant, a colloidal protective agent, and a polyphosphoric acid alkali metal salt. JP-A-01095102 discloses a combination of PVA, gelatin or cellulose derivatives with a specific copolymer of carbon monoxide and (meth)acrylate containing anionic or cationic groups. EP-A-0 492 712 discloses the use of 20 polyether polysiloxanes or a water-soluble copolymer of a C₈-C₂₄ α-olefin and a specific α,β-unsaturated dicarboxylic acid ester in order to enable the production of finely divided peroxide dispersions. However, since the ingredients of the suspensions are not fully compatible with the polymerization process in which the suspensions are eventually used, 25 these formulations also are generally not acceptable.

Therefore, the main disadvantage of the described suspensions of thermally labile organic compounds is that they suffer from production problems, do not fulfill storage stability requirements and/or are not

universally applicable in polymerization processes. More specifically, it is observed that some storage stable peroxide suspensions can be produced according to the prior art, but when they are used in vinyl chloride (co)polymerization, one or more properties of the resulting polymer is not
5 acceptable.

In respect of applicability in vinyl chloride (co)polymerization processes, it is noted that current initiator suspensions have an effect on the polymer morphology, for instance porosity, the electrical properties of the polymer,
10 and the fish eye level. Further, these initiator suspensions typically suffer from other disadvantages, such as high viscosities, which make them difficult to handle, or in some cases the suspensions cannot be milled to reduce the particle size of the organic compound. A reduction of the peroxide concentration in order to reduce the viscosity and/or the milling
15 problems often is not acceptable from an economic point of view.

Accordingly, there still is a need for improved peroxide suspensions and an improved process to make them. More specifically, there is a need for improved, chemically and physically stable, compositions of thermally labile
20 organic compounds which are generally applicable in polymerization processes, particularly in the polymerization process of vinyl chloride monomer. The improved compositions are to combine a high concentration of the thermally labile organic compound with an acceptable viscosity, with the thermally labile organic compound having a small average particle size,
25 and are not to affect the properties of the polymer produced therewith. These and other objects of the present invention will be apparent from the summary and the detailed description which follow.

Summary of the invention

After many years of intensive research and development in the field of suspensions and emulsions of thermally labile organic compounds, we
5 have now found compositions that fulfill all or most of the above-identified requirements and which can be produced by means of conventional milling techniques.

The present invention relates, in a first embodiment, to a process to
10 prepare an aqueous suspension comprising:

- from 5 to 60% by weight of the total formulation of one or more solid thermally labile organic compounds,
- 0.5-10% by weight of the total formulation of one or more polyvinyl alcohols having an average degree of hydrolysis from 60 to less than 80%,
15 with the proviso that no polyvinyl alcohol with a degree of hydrolysis of less than 55% is employed
- 0.05 to 1% by weight of the total formulation of one or more emulsifiers having an average HLB value from 14.5 to 20.0,
wherein at least one solid thermally labile organic compound is milled in
20 water.

The present invention, in a second embodiment, relates to suspensions of bis(4-tert-butylcyclohexyl) peroxydicarbonate, dimyristyl peroxydicarbonate and/or lauric peracid that are obtainable by said process.
25

In a further embodiment, the invention relates to a process for the polymerization of vinyl chloride alone or in admixture with up to 40 weight percent of one or more ethylenically unsaturated monomers copolymerizable therewith, oligomers or (co)polymers of the

aforementioned monomers, and mixtures of one or more of the monomers, oligomers, and (co)polymers, characterized in that a peroxidic polymerization initiator and/or chain transfer agent is used in the form of an aqueous suspension as set forth above.

5

These and other aspects will be discussed in more detail in the following description and examples.

10 Detailed description of the invention

According to the first aspect of the present invention a process is provided to prepare aqueous suspensions of thermally labile organic compounds by milling and/or homogenizing the solid peroxide in an aqueous medium 15 preferably comprising one or more particular protective colloids or one or more emulsifiers. More preferably, the aqueous medium comprises one or more particular protective colloids and one or more emulsifiers. The term "thermally labile organic compound," as used in this specification, defines compounds that will form free radicals upon thermal decomposition. This 20 class of compounds encompasses organic peroxides, azo-initiators, C-C initiators, NO-compounds, and peroxydicarboxylic acids. Preferred compounds for use in the present invention are organic peroxides and azo-initiators. More preferred are organic peroxides.

25 More particularly, preferred organic peroxides for use in the present invention are diacyl peroxides, peracids, and peroxydicarbonates. More preferred are peroxides selected from dicyclohexyl peroxydicarbonate, bis(4-tert-butylcyclohexyl) peroxydicarbonate, dimyristyl peroxydicarbonate, dicetyl peroxydicarbonate, didecyl peroxydicarbonate, didecanoyl peroxide,

dilauroyl peroxide, lauric peracid, and mixtures thereof. More preferred still are suspensions of bis(4-tert-butylcyclohexyl) peroxydicarbonate, dimyristyl peroxydicarbonate, and/or lauric peracid. The most preferred organic peroxide formulated according to the invention is bis(4-tert-butylcyclohexyl) peroxydicarbonate. This particular peroxide shows an unacceptable thermal decomposition rate when melted and cannot be processed or formulated in ways involving a melting step. However, also for the other preferred compounds the process according to the invention, where the peroxide is milled/homogenized in the solid state, is preferred from a safety point of view.

The amount of thermally labile organic compounds to be used in the process to make the aqueous suspension usually falls in the range of 5-60% by weight, based on the weight of the suspension. Preferably, 20-50% by weight of the compound is present. Most preferred are concentrated suspensions where the thermally labile organic compound is present in a concentration of 35-50% by weight. At concentrations of less than 5% by weight the cost of transportation becomes prohibitive and at concentrations above 60% by weight the products cannot be handled easily and may even be unsafe.

The storage stability of the suspension made in the process according to the invention, preferably is greater than 2 months, more preferably more than 3 months.

25

The Brookfield viscosity of the suspension that is made in the process according to the invention, preferably is between 750 to 5000 mPa.s, more preferably between 750 and 3750 mPa.s. More preferably still, such a Brookfield viscosity is combined with an Erichsen viscosity from 50 to 250

mPa.s. Most preferred are suspensions with a Brookfield viscosity from 1000 to 2500 mPa.s and an Erichsen viscosity from 70 to 150 mPa.s.

The particle size of the thermally labile organic compound in the
5 suspension is preferably very small, in order to obtain all desired properties
of both the suspension and the polymers prepared in processes where the
suspension is used. Therefore, the d_{90} of the particle size distribution is
preferably less than 20 μm . More preferred are suspensions where the
organic compound has a particle size distribution with a d_{90} within the range
10 of 0.1-15 μm . The most preferred suspensions are characterized by a d_{90}
below 10 μm .

In the process according to the invention, use is made of an aqueous
medium in which the thermally labile organic compound is dispersed. This
15 aqueous medium preferably comprises from 0.5 to 20% by weight of at
least one specific polyvinyl alcohol as the protective colloid (based on the
total weight of the suspension). More preferably, the colloid makes up 1 to
10% by weight, most preferably from 1 to 5% by weight, of the total
formulation.

20 More particularly, the specific polyvinyl alcohols (PVAs) that can be used in
the compositions according to the invention are saponified polyvinyl
acetates with a degree of hydrolysis of between 60 and 80%. Preferably,
the degree of hydrolysis of the PVA is from 62 to 78%. If more than one
25 PVA is used, the indicated degree of hydrolysis is generally the weight
averaged degree of hydrolysis of the products used, with the proviso that
all PVA must have a degree of hydrolysis greater than 55%. Although the
PVAs may be combined with other known colloids, it is preferred to use the
referenced PVAs exclusively.

The emulsifiers used in the compositions that can be produced according to the present invention are characterized by their HLB value being from 14.5 to 20.0. The HLB value is indicative of the hydrophilic-lipophilic balance, as described in "The Atlas HLB-system, a time saving guide to emulsifier selection" published by Atlas Chemical Industries Inc., 1963. For blends of emulsifiers the HLB value is the weight average HLB value of the components. Preferably, emulsifiers with an HLB value from 15.7 to 20.0 are used. More preferred are emulsifiers with an HLB value from 16.9 to 10 20.0. More preferred still are emulsifiers with an HLB value from 17.8 to 20.0. Most preferred are fatty alcohol ethoxylates and fatty ester ethoxylates with an HLB value in the indicated range. Less preferred emulsifiers are the ethoxylated sorbitan esters since they often lead to problems in respect of the storage stability of the suspension. Typically, the 15 emulsifiers are used in a concentration less than 1% by weight of the total formulation. Preferred are emulsifier concentrations from 0.05 to 0.8 % by weight of the total formulation.

In the process according to the invention, the aqueous medium may further 20 comprise one or more thickeners in a concentration up to 2% by weight of the total formulation. Preferably, the thickener makes up less than 1% by weight of the suspension. Non-limiting examples of thickeners useful in the formulation are xanthane gum, Arabic gum, and alginates.

25 Further, other standard additives, including pH-adjusting agents such as calcium oxide or phosphate buffers, sequestering agents, and, if desired, biocides, e.g. fungicides, can be used. The concentration of these additives will depend on the desired effect and the other ingredients in the suspension. Given the information presented here, the skilled man will

have no problem in selecting appropriate concentrations of the individual ingredients in the suspension of choice.

All of the ingredients listed above preferably are part of the aqueous
5 medium in which the solid thermally labile organic compound is dispersed.
However, one or more of the ingredients may also be added after the
dispersion step of the thermally labile organic compound. In that case, it is
preferred to make a suspension with a higher than desired concentration of
the thermally labile organic compound(s) which is then subsequently
10 diluted with a concentrated solution of the required ingredient.

The temperature of the aqueous medium prior to the
millling/homogenization step is preferably below the lowest recommended
storage temperature of the solid thermally labile organic compound(s)
15 being dispersed. More preferably, the processing temperature is between 0
and 15°C. Most preferred is a temperature between 0 and 5°C. Lower
temperatures are not very economical and may call for the use of
undesired anti-freeze agents, while higher temperatures can result in
undesired decomposition of the initiator.

20 The primary advantage of the present invention is that it provides a process
to make chemically and physically stable, low viscous, concentrated
suspensions of a thermally labile organic compound with a small average
particle size and a good particle size distribution, which can be used in vinyl
25 chloride polymerizations without affecting the electrical properties of the
polymer. Preferred suspensions of said thermally labile organic compound
mainly contain one or more PVAs as the protective colloid and minor
quantities of one or more non-ionic emulsifiers. Therefore, the suspensions
of the present invention do not adversely affect polymerization processes

or any property of the resultant polyvinyl chloride (PVC). These suspensions can actually improve properties such as the fish eye level and the morphology of the resultant polymer. Hence, the suspensions according to the present invention enable the use of polymerization 5 initiators which are efficient, easy to handle, and have a favourable effect on the polymer produced with them.

The process involves, preferably, a first mixing step in which the thermally labile organic compound is stirred into an aqueous medium comprising 10 emulsifier(s) and protective colloid(s) to form a mixture; this mixture preferably is then milled to form a coarse suspension, after which, preferably, the compound is more finely divided by further milling or homogenization. If and when a thickener, pH stabilizer or other ingredient is used in the formulation, it may be added at any point in the production 15 process. Preferably, such an ingredient is added in the form of a concentrated solution.

The mixing step only requires the use of a stirrer of any conventional type. For the step to form the coarse suspension typically use is made of a high 20 shear mixer, for instance a colloid mill, high-shear rotor-stator mixers, high-speed pump, etc.. Milling the coarse dispersion to further reduce the particle size of the thermally labile organic compound can be done by any equipment that is able to induce still higher shear forces, or by impact mills. Examples of such suitable equipment include, high-frequency and 25 ultrasonic oscillators, perl mills, roller mills, and homogenizers. Given that concentrated suspensions with partially saponified polyvinyl acetate were typically found to form a thick paste during milling, it is surprising and unexpected that such a milling process can be carried out in a convenient way on the concentrated suspensions of the present invention.

In a second embodiment, the invention relates to suspensions of bis(4-tert-butylcyclohexyl) peroxydicarbonate, dimyristyl peroxydicarbonate and/or lauric peracid that are obtainable by the above-mentioned process. Most 5 preferred are suspensions of bis(4-tert-butylcyclohexyl) peroxydicarbonate. Until now, these suspensions could not be produced without substantial decomposition (in a melting process) or without a concentrated, low-viscous, storage stable suspension with small particle size being formed (milling process), or without the properties, such as morphology or electrical 10 conductivity, of the polymer produced being adversely influenced.

The present invention also relates to a polymerization process where at least one of the above-described suspensions is used as (one of) the polymerization initiator(s) and/or chain transfer agent(s) in the 15 polymerization of vinyl chloride alone or in admixture with up to 40 weight percent of one or more ethylenically unsaturated monomers copolymerizable therewith, oligomers and (co)polymers of the aforementioned monomers, and mixtures of two or more of these monomers, oligomers, and polymers. The use of these suspensions is 20 further detailed below.

The polymerizable monomers for the present polymerization process include vinyl halides, particularly vinyl chloride, and ethylenically unsaturated monomers having at least one terminal unsaturated group. 25 Examples of such ethylenically unsaturated monomers include esters of acrylic acid such as methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate, cyanoethyl acrylate, and the like, esters of methacrylic acid such as methyl methacrylate, butyl methacrylate, and the like, styrene and styrene derivatives including α -methylstyrene, vinyl toluene, chlorostyrene

and the like, acrylonitrile, ethyl vinyl benzene, vinyl acetate, vinyl naphthalene, etc., and di-olefins including, but not limited to, butadiene, isoprene, chloroprene, and the like, and other ethylenically unsaturated monomers known to those of ordinary skill in the art.

5

In addition, oligomers and polymers made from one or more of the above-identified monomers may also be reacted with other monomers, polymers or oligomers in the present polymerization process. Of course, mixtures of two or more of the polymerizable materials can be used. In all cases there
10 will be at least 60% of vinyl chloride monomer, oligomer or polymer in the polymerizable mixture.

Generally, a polymerizable composition comprises 0.01-6.0% by weight of one or more thermally labile organic compounds (initiators), based on the
15 polymerizable monomers, and when polymerizing vinyl chloride alone, preferably 0.01-0.3% by weight of the initiator, based on the monomer. If one or more of the initiators are in the form of a composition according to the invention, the amount of the composition is to be chosen such that the indicated amount of pure initiator is supplied. When peracid suspensions
20 according to the invention are used as an initiator, a chain transfer agent or as a combined initiator and chain transfer agent in a vinyl chloride polymerization process, such suspensions may also be combined with the aforesaid initiator suspensions. Chain transfer agents are typically employed in a concentration of between 0.001 and 10.0% by weight of
25 pure chain transfer agent, based on the polymerizable materials. Preferably, from 0.01 to 1% by weight of these chain transfer agents is used.

A significant advantage of the present process for the polymerization of vinyl chloride is that the use of suspensions of the present invention leads to greater flexibility in the polymerization process itself. More particularly, when the present solid peroxide compositions according to the state of the art are used in vinyl chloride polymerization, the peroxide composition must be added to the polymer before the mixture is brought to the polymerization temperature in order to avoid adverse effects, such as increased fish eye levels, on the properties of the resultant polymer. However, in the process of the present invention, the polymerization initiator may be added to the vinyl chloride monomer after it is heated to the polymerization temperature or may even be dosed stepwise or gradually during the polymerization reaction. These features provide greater flexibility in the polymerization process as well as a means of gaining better control over the process and the products of the process.

15

The polymerization process of the present invention typically is a suspension polymerization process in which an aqueous dispersion of vinyl chloride monomer and the polymerization initiator are heated to cause polymerization of the monomer as a result of free radical decomposition of the polymerization initiator. However, the suspensions obtainable by the process according to the invention can also be used in a so-called "mass polymerization" process. The polymerization conditions employed are the conventional conditions for vinyl chloride monomer polymerization. For a detailed description of the process conditions, as well as the types of monomers which can be polymerized by this method, reference may be made to US 3,825,509, which is incorporated herewith by reference.

The present polymerization process, however, may differ slightly from that of US 3,825,509 in that it is not necessary to add the ingredients to the polymerization reactor in the order of water, dispersant, polymerization initiator, and, finally, monomer. While this conventional methodology is

5 within the scope of the present invention, the present invention also encompasses reactions where the water, the dispersing agent, and the monomers are added to the reactor and heated to the polymerization temperature prior to the introduction of the polymerization initiator. In such reactions the polymerization initiator is added all at once, gradually or

10 stepwise during the polymerization process.

Previously, it was considered disadvantageous to add a solid polymerization initiator at the reaction temperature, since the fish eye level would then increase to unacceptable levels. In the examples which follow it

15 is demonstrated that the present suspensions do not significantly increase the fish eye level. Furthermore, dosing at reaction temperature may allow a better control of the polymerization rate in the polymerization process.

The polymerization process according to the invention results in polymers

20 which exhibit desirable properties, including better electrical properties, lower fish eye levels, and, in some instances, improved polymer morphology, such as porosity.

The following examples are provided to further illustrate the present

25 invention and are not to be interpreted as limiting the invention in any way.

Experimental

Materials:

The following PVAs were used:

- 5 Polyviol® M05/190 ex Wacker (approx. 82.5% hydrolysis)
Gohsenol® KH20 ex Nippon Gohsei (approx. 80% hydrolysis)
Polyviol® V03/240 ex Wacker (approx. 77% hydrolysis)
Gohsenol® KP08 ex Nippon Gohsei (approx. 73% hydrolysis)
Alcotex® 72.5 ex Harco (approx. 72.5% hydrolysis)
- 10 Ethapol® 66 ex CIRS (approx. 66% hydrolysis, microemulsion)
Polyvic® SP808 ex 3V (approx. 65% hydrolysis)
Unitika® UMR10M ex Unitika Chemical (approx. 65% hydrolysis)
Alcotex® 552P ex Harco (approx. 55.5% hydrolysis)
Gohsenol® LL02 ex Nippon Gohsei (approx. 48% hydrolysis)

15

The following non-ionic emulsifiers were used:

- Berol® 08 ex Berol Nobel (HLB = 18.7)
- Igepal® CO897ex GAF (HLB = 17.8)
- Brij® 35 ex ICI (HLB = 16.9)
- 20 Brij®58 ex ICI (HLB = 15.7)
- Cedepal® E710 ex Domtar (HLB = 14.4)
- Elfapur® T110 ex Akzo Nobel (HLB = 13.5)

25 The thickener employed was a xanthane gum, Rhodigel® 23, supplied by Rhone Poulenc.

Bis(4-tert-butylcyclohexyl) peroxydicarbonate (Perkadox® 16), dicetyl peroxydicarbonate (Liladox® 90P) and dimyristyl peroxydicarbonate (Perkadox® 26) were supplied by Akzo Nobel and used as an initiator.

VCM was of polymerization grade, while all other materials were standard chemicals of reagent grade. These compounds were used without further purification.

5 Procedures:

1. Suspensions were prepared by mixing the thermally labile organic compound in the aqueous phase containing the other ingredients in the proper ratio, with a turbine-type stirrer, at 10°C. Subsequently, the mixture was first dispersed with an Ultra-Turrax® rotor-stator dissolver for 5 minutes at 700 W stirring energy per kg of mixture, to form coarse suspensions and next milled with a 500 ml Drais® Perl Mill PM1. The perl mill was filled with 1-2 mm glass beads for 80% by volume. The coarse suspensions were milled at a rate of 400 ml/min at a temperature of 10°C maximum, preferably 5°C. Finally, the suspensions were deaerated.
10
- 15 2. The suspensions were characterized in terms of viscosity, particle size (distribution), and physical stability on aging (separation). The viscosity was determined with an Erichsen® Viscometer, type 332-1 and a Brookfield® LVT viscometer at 12 rpm, spindle 3. The particle size (distribution) was determined by light scattering techniques using a Malvern® Particle Sizer M3. Separation of the suspensions was determined visually by storing in 500 ml HDPE jars.
20
- 25 3. The polymerization reactions were carried out in a one-litre Büchi stainless steel autoclave with stirrer and baffle. The reactor was filled with aqueous protective colloid solution in which the phosphate buffer was dissolved. Depending on the tests to be performed (see below), one of the following methods was used:
25

3.1 A suspension of the thermally labile organic compound was added in an amount of 0.07% pure peroxide, based on the vinyl chloride monomer. The reactor was then evacuated and flushed with nitrogen four times while stirring. After addition of the VCM, the mixture was heated to reaction
5 temperature (53.5°C) in 60 minutes.

3.2 The reactor was evacuated and flushed with nitrogen four times while stirring. Then VCM was mixed in at room temperature and the reaction mixture was heated, in 25 minutes, to 53.5°C. Subsequently, the
10 suspension of the thermally labile organic compound was added in an amount of 0.07% pure peroxide, based on the vinyl chloride monomer, by means of an appropriate syringe through a septum.

For both methods the reactor was cooled after 6 hours of polymerization
15 time and excess vinyl chloride monomer was vented. The polyvinyl chloride was filtered, washed, dried overnight at 50°C, weighed, and analyzed. The conversion of the vinyl chloride monomer was determined by gravimetric analysis.

20 4. The DOP porosity and the volume resistivity of the PVC were determined by analyzing material from method 3.1, in accordance with DIN 53417 (centrifuge method) and ASTM D257-66 (22°C, 46% R.H.), respectively.

5. The fish eye level, particle size (distribution), and bulk density were analyzed in conventional ways on PVC obtained by method 3.2. The fish eye level was determined in accordance with the method of O. Leuchs, *Kunststoffe*, 50(4) 1960, pp. 227-234. Preferably, the fish eye 5 level is as low as possible. The polyvinyl chloride mean particle size was determined with a Coulter Counter® (multisizer), and the bulk density was determined in a conventional way by means of an Erichsen DIN cup 243/11.8.

10 Example 1

A suspension was prepared containing 2% by weight of Alcotex 72.5 (approx. hydr. 72.5%), 0.3% by weight of Igepal CO897 (HLB 17.8), 0.15% by weight of xanthane gum, 0.05% by weight of CaO, 40% by weight of 15 Perkadox 16, the remainder being demineralized water.

The suspension showed excellent physical and chemical stability during more than 3 months of storage and had the following properties:

d ₅₀ (μm)	5
20 d ₉₀ (μm)	12
Erichsen viscosity (mPa·s)	140
Brookfield viscosity (mPa·s)	1530

20

The PVC produced using this suspension had the following properties:

DOP porosity (%)	22
vol.resistivity (Ωcm)	$14 \cdot 10^{13}$
fish eyes (m^{-2})	30
5 average particle size (μm)	160
bulk density ($\text{g}\cdot\text{ml}^{-1}$)	0.40

Example 2

10

Example 1 was repeated, except that Polyviol V03/240 (approx. hydr. 78%) was substituted for the Alcotex 72.5 and 0.4% of Berol 08 (HLB 18.7) was used instead of the 0.3% Igepal CO897. The suspension had the following properties:

15	d50 (μm)	4.8
	d90 (μm)	10.5
	Erichsen viscosity ($\text{mPa}\cdot\text{s}$)	160
	Brookfield viscosity ($\text{mPa}\cdot\text{s}$)	4950.

The suspensions were storage stable for at least 3 months.

20

Example 3

A suspension was prepared containing 2% by weight of Unitika UMR10m
25 (approx. hydr. 65%), 0.3% by weight of Berol 08 (HLB 18.7), 0.15% by weight xanthane gum, 0.05% by weight CaO, 40% by weight of Perkadox 16, the remainder being demineralized water.

The suspension showed excellent physical and chemical stability during more than 6 months of storage and had the following properties:

d ₅₀ (μm)	4
d ₉₀ (μm)	9
5 Erichsen viscosity (mPa·s)	130
Brookfield viscosity (mPa·s)	1800

The PVC produced using this suspension had the following properties:

10 DOP porosity (%)	24
vol.resistivity (Ωcm)	12·10 ¹³
fish eyes (m ⁻²)	25
average particle size (μm)	155
bulk density (g·ml ⁻¹)	0.40

15

Example 4

A suspension was prepared containing 1.5% by weight of Polyvic SP808
20 (approx. hydr. 65%), 0.6% by weight of Brij 35 (HLB 16.9), 0.15% by weight xanthane gum, 0.05% by weight CaO, 40% by weight of Perkadox 16, the remainder being demineralized water.

The suspension had the following properties:

25 Erichsen viscosity (mPa·s)	170
Brookfield viscosity (mPa·s)	4120

The product was storage stable for at least 3 months.

Comparative Example A

Example 1 was repeated, except that this time the suspension consisted of 1.5% by weight of Gohsenol KP08 (approx. hydr. 73%), 0.15% by weight of 5 xanthane gum, 0.05% by weight of CaO, 40.0% by weight of Perkadox 16, and 58.25% by weight of water, with the following results.

The suspension was physically and chemically stable during less than 8 weeks of storage and had the following properties:

10	d ₅₀ (μm)	6
	d ₉₀ (μm)	19
	Erichsen viscosity (mPa·s)	220
	Brookfield viscosity (mPa·s)	3600

15	The PVC produced using this suspension had the following properties:	
	DOP porosity (%)	22
	vol.resistivity (Ωcm)	15•10 ¹³
	fish eyes (m ⁻²)	> 5,000
	average particle size (μm)	145
20	bulk density (g•ml ⁻¹)	0.40

Comparative Example B

Example 1 was repeated, except that Alcotex 552P (average hydrolysis 55.5% but with a substantial amount of material with a degree of hydrolysis 5 below 55%) was substituted for the Alcotex 72.5 and the Igepal CO897 was replaced with Berol 08 (HLB 18.7).
The resulting suspension was very thixotropic and showed unacceptable storage and handling properties.

10

Comparative examples C and D

Example 3 was repeated, except that the Berol 08 was replaced with Cedepal E710 (HLB 14.4) and Elfapur T110 (HLB 13.5) in Examples C and 15 D, respectively. Both suspensions were too thick to be handled easily.

Comparative Example E

20 Example 3 was repeated, except that 1% by weight of Gohsenol LL02 (approx. hydr. 48%) and 1% by weight of Polyviol M05/190 (approx. hydr. 82.5%) were substituted for the 2% by weight of Unitika UMR10m.
The resulting suspension was not storage stable. After two weeks it was too thick to be handled easily.

25

Comparative Example F

Example 1 was repeated, except that Gohsenol KH20 (approx. hydr. 80%) was substituted for the Alcotex 72.5. This suspension was too thick to be
5 processable. No representative sample was attainable.

Comparative Example G

Example 3 was repeated, except that Ethapol 66 (approx. hydr. 66%) was
10 substituted for the Unitika UMR10m. The Ethapol is a mixture of PVAs with low (46%) and high (>76%) degrees of hydrolysis.
This suspension was too thick to be handled easily.

Examples 5-6

15

The experiment of Example 1 was repeated, except that the Igepal CO897 was replaced with another non-ionic emulsifier, as indicated in the following table.

Example	Non-ionic emulsifier	HLB value	Erichsen visc. (mPa·s)	Brookfield (mPa·s)
5	Brij 35	16.9	120	1350
6	Brij 58	15.7	160	1820

20

The products were storage stable.

Example 7

A suspension was prepared according to procedure 1, using 40% by weight of Perkadox 26, 2.0% by weight of Alcotex 72.5, 0.3% by weight of Berol

5 08, 0.17% by weight of xanthane gum, and 57.53% by weight of water.

The suspension showed excellent physical and chemical stability during more than 3 months of storage and had the following properties:

d_{50} (μm) 8.6

10 d_{90} (μm) 20.0

Erichsen viscosity (mPa·s) 90

Brookfield viscosity (mPa·s) 1920

Example 8

15

A suspension was prepared according to procedure 1, using 44.44% by weight of Liladox® 90P (equivalent to 40% by weight of dicetyl peroxydicarbonate), 2.0% by weight of Unitika UMR 10M, 0.7% by weight of Berol 08, 0.15% by weight of xanthane gum, 0.08% by weight of sodium dicarbonate, and 52.63% by weight of water.

The suspension showed good physical and chemical stability during more than 3 months of storage, and had the following properties:

d_{50} (μm) 5.3

25 d_{90} (μm) 19.9

Erichsen viscosity (mPa·s) 75

Brookfield viscosity (mPa·s) 1630

Claims

1. A process to prepare an aqueous suspension comprising:
 - from 5 to 60% by weight of the total formulation of one or more solid thermally labile organic compounds,
 - 0.5-10% by weight of the total formulation of one or more polyvinyl alcohols having an average degree of hydrolysis from 60 to less than 80%, with the proviso that no polyvinyl alcohol with a degree of hydrolysis of less than 55% is employed
 - 0.05 to 1% by weight of the total formulation of one or more emulsifiers having an average HLB value from 14.5 to 20.0, wherein at least one solid thermally labile organic compound is milled in water.
- 15 2. A process according to claim 1, wherein at least one solid thermally labile organic compound is milled in an aqueous medium, which medium comprises at least one of said polyvinyl alcohols or at least one of said emulsifiers.
- 20 3. A process according to claim 1 or 2, wherein the thermally labile organic compound is selected from diacyl peroxides, peracids, peroxydicarbonates, and mixtures thereof.
- 25 4. A process according to claim 3, wherein the thermally labile organic compound is dicyclohexyl peroxydicarbonate, bis(4-tert-butylcyclohexyl) peroxydicarbonate, dimyristyl peroxydicarbonate, dicetylperoxy peroxydicarbonate, didecyl peroxydicarbonate, didecanoyl peroxide, dilauroyl peroxide, or lauric peracid, or a mixture of two or more of these compounds.

5. A process according to any one of claims 1-4, wherein the particle size distribution of the thermally labile organic compound in the final suspension has a d_{90} of less than $20\mu\text{m}$.
- 10 7. A process according to any one of the preceding claims, wherein the degree of hydrolysis of the polyvinyl alcohol is from 62 to 78%.
8. A process according to any one of the preceding claims, wherein the emulsifier has an average HLB value from 16.9 to 20.0.
- 15 9. A process according to any one of the preceding claims wherein the concentration of the thermally labile organic compound is from 35 to 45% by weight, the concentration of the polyvinyl alcohol is from 1 to 5% by weight, and the concentration of the emulsifier is from 0.05 to 20 0.8% by weight, all based on the total weight of the formulation.
10. A process according to any one of the preceding claims, wherein the final suspension further comprises a thickener in a concentration up to 2% by weight of the total formulation.
- 25 11. A process according to any one of the preceding claims, wherein the final suspension further comprises one or more additives selected from pH-adjusting agents, sequestering agents, and biocides.

12. A process according to any one of the preceding claims, wherein the process involves a mixing step and at least one milling step during which the temperature is controlled, preferably at a temperature below 10°C.
5
13. A suspension of bis(4-tert-butylcyclohexyl) peroxydicarbonate, dimyristyl peroxydicarbonate, lauric peracid, or a mixture thereof, obtainable by a process according to any one of claims 1-12.
- 10 14. A suspension according to claim 13 comprising bis(4-tert-butylcyclohexyl) peroxydicarbonate as the sole thermally labile organic compound.
- 15 15. A polymerization process wherein vinyl chloride, optionally together with up to 40% by weight of ethylenically unsaturated comonomers, is polymerized using one or more thermally labile organic compounds, characterized in that an aqueous suspension is used that is obtainable by the process as defined in any one of claims 1-12.
15
- 20 16. A polymerization process according to claim 15, characterized in that an aqueous suspension is used comprising just bis(4-tert-butylcyclohexyl) peroxydicarbonate as the thermally labile organic compound.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/05919

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F218/08 C08F14/06 C07C409/00

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 492 712 A (AKZO NV) 1 July 1992 cited in the application * see examples 4-6 ; page 6, line 3 * see page 3, line 15 - page 4, line 31; examples 1-3,7-23 ---	1-16
X	GB 2 068 008 A (KENOGARD AB) 5 August 1981 * see page 2, line 13-53 ; examples 1-6 ; page 1, line 50 - page 2, line 12 * see page 3, line 59 - page 4, line 5 ---	1-4,7-16
X	EP 0 385 734 A (SUMITOMO CHEMICAL CO) 5 September 1990 * abstract * see column 2, line 39 - column 3, line 34; examples 1-12 ---	1,2,5-9, 11,12,15 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the International search report
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INTERNATIONAL SEARCH REPORT

Inte	nal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	EP 0 517 290 A (BEROL NOBEL AB) 9 December 1992 see examples 13,14 -----	1-16

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